Department of Pesticide Regulation

Mary-Ann Warmerdam
Director

MEMORANDUM

Edmund G. Brown Jr.
Governor

TO: Randy Segawa
Environmental Program Manager I
Environmental Monitoring Branch

Original signed by Frank Spurlock for

FROM: Daniel R. Oros, Ph.D.
Environmental Scientist
Environmental Monitoring Branch

Frank C. Spurlock, Ph.D.
Research Scientist III
Environmental Monitoring Branch
916-324-4124

Original signed by

DATE: January 28, 2011

SUBJECT: ESTIMATING PESTICIDE PRODUCT VOLATILE ORGANIC COMPOUND OZONE REACTIVITY. PART 2: REACTIVITY-WEIGHTED EMISSIONS

ABSTRACT

In this memorandum we (a) describe a procedure for estimating ozone (O_3) formation potential of pesticide products, (b) compare 1990 and 2007 ozone season pesticide O_3 formation potentials in the San Joaquin Valley (SJV), (c) compare the relative contribution of individual product components to SJV O_3 formation potentials, (d) compare the relative contribution of different products to SJV O_3 formation potentials, and (e) compare SJV O_3 formation potentials based on both the maximum incremental reactivity (MIR) and equal benefit incremental reactivity (EBIR) scales. As used here, ozone formation potential (OFP) *does not* refer to actual O_3 produced, but is instead a *relative* measure of reactivity-weighted mass Volatile Organic Compound (VOC) emissions. (Note: A full listing of all acronyms is given in Appendix 1 at the end of this paper.)

Although SJV VOC mass emissions were approximately 15% lower in 2007 than 1990, differences were smaller for total ozone season SJV OFPs as determined on either the MIR or EBIR scales. In 1990, the estimated MIR OFP was 58.9 tons per day O_3 equivalents (tpdoe) and the EBIR OFP was 12.5 tpdoe. In 2007 the MIR OFP was 55.2 tpdoe while the EBIR OFP was 11.8 tpdoe. Nonfumigant products were greater contributors to total SJV OFP in both years than fumigants. The estimated nonfumigant product OFP contribution was 58.2 and 44.9 tpdoe (MIR basis) and 12.1 and 9.1 tpdoe (EBIR basis) in 1990 and 2007, respectively. The biggest difference between 1990 and 2007 was the change in the relative contribution of fumigants to SJV ozone season OFPs; the MIR OFP increased markedly from 0.7 tpdoe in 1990 to 10.3 tpdoe in 2007, while the EBIR OFP was 0.4 tpdoe as compared to 2.7 tpdoe in 2007. That difference between years was primarily attributable to increased use of 1,3-dichloropropene (1,3-D) in 2007 with a concommitant decrease in methyl bromide use. 1,3-D has relatively high reactivity while that of methyl bromide is very low. Of the nonfumigant products investigated, the largest contributor to

OFP were a group of five subregistered/label revision emulsifiable concentrate (EC) chlorpyrifos products. These 5 products yielded a combined 2007 OFP of 13.5 tpdoe (MIR basis) and 2.5 tpdoe (EBIR basis). The highest contributing nonfumigant product in 1990 was an EC formulation of the cotton defoliant S,S,S-tributyl phosphorotrithioate (tribufos). In all 3 cases (1,3-D, chlorpyrifos and tribufos), the high OFPs relative to other products was attributable to three factors: high product emission potentials (EPs), high component ozone reactivities, and high product use. The combination of high reactivity and high use was also a characteristic of the highest contributing individual product component VOCs. Based on speciation of the representative nonfumigant products, in 2007 the highest OFP contributing nonfumigant product components were aromatic 100, aromatic 150, aromatic 200 and acrolein.

1. INTRODUCTION

California's State Implementation Plan (SIP) for the federal Clean Air Act includes a pesticide element that requires the Department of Pesticide Regulation (DPR) to track VOC emissions for agricultural and structural pesticides. The current pesticide VOC inventory is a mass-based inventory that tracks pounds of VOCs emitted from agricultural and commercial structural pesticide applications. The inventory does not account for differences among VOCs in their ability to participate in tropospheric O_3-forming reactions. DPR recently proposed a pilot study to evaluate the scientific issues and uncertainties associated with incorporating reactivity in DPR's emission inventory, and identify potential approaches to resolving these issues. (Oros, 2009). One objective of the pilot study was to estimate the relative O_3 reactivity of individual pesticide products. This memorandum is Part 2 of the pilot study. Part 1 focused on identification of volatile components (speciation) of pesticide products (Oros and Spurlock, 2010). As part of that effort, pesticide product EPs were estimated from Confidential Statements of Formula (CSF), and the estimation procedure then verified by comparison of CSF-estimated EPs to thermogravimetric analysis (TGA) measured EPs (Oros and Spurlock, 2010). The agreement between measured and estimated product EPs indicated accurate identification of the volatile components in each product.

In contrast to the mass of VOCs emitted from a product, in this paper we introduce the specific ozone formation potential of a product (SOFP), (mass O_3 equivalents/mass product) and the ozone formation potential [OFP, mass O_3 equivalents). The SOFP is a *relative* measure of a product's ability to form ozone expressed on a per mass product basis, and is calculated according to the specific Incremental Reactivity (IR) reference scale chosen. An appropriate use of SOFP is to compare relative O_3-forming potential among different products.

The OFP is a *relative* measure of ozone formation from one or multiple pesticide applications, and is a measure of reactivity-weighted mass VOC emissions expressed in terms of O_3 equivalents. The OFP accounts for product SOFP, but also includes the amount of product actually applied and the application method adjustment factor (AMAF; Barry et al., 2007).

Appropriate uses of OFP include comparisons of mass of reactivity-weighted emissions across years, between different regions, or from different pesticide products or crops. Like the SOFP, OFPs are defined relative to a chosen reference IR scale.

One commonly used IR scale is the Maximum Incremental Reactivity scale (MIR) (Carter, 1994, 2009a, 2009b). When the MIR scale is chosen as a reference scale, the MIR SOFP is an estimate of the mass of O_3 formed by unit product mass *under MIR conditions*. "MIR conditions" refers to a standard scenario defined by conditions where (a) there is a defined ratio of VOC:NOx (oxides of nitrogen) and (b) the VOC composition is standardized (a so-called "base VOC mixture"). Generally speaking, MIR conditions are representative of relatively high NOx conditions where VOC emissions have the greatest effect on O_3 formation (Carter, 1994). They are typically most representative of urban conditions. An alternate IR is the EBIR scale. The EBIR SOFP is an estimate of the mass of O_3 formed by unit product mass *under EBIR conditions*. "EBIR conditions" are those with lower NOx concentrations such that O_3 formation is equally sensitive to concentration changes of either NOx or VOC (so-called "equal benefit", Carter, 1994). The individual chemical reactivities in either IR scale have units of (mass O_3/mass VOC; Carter, 1994). However, it is critical to recognize that the SOFP and OFP <u>do not represent the actual quantity of O_3 formed from pesticide product use</u> because MIR conditions or EBIR conditions do not generally represent actual tropospheric conditions at the time of application. For this reason, SOFP and OFP should be considered *relative* metrics that describe potential O_3 formation. While incremental reactivities of chemicals expressed on the EBIR and MIR scales differ, they are highly correlated, demonstrating their similarity on a relative basis. Consequently, if a chemical displays a high reactivity on one scale, it will also generally display a high reactivity on another scale. Similarly, we will show that if a product possesses a relatively high SOFP on one reference IR scale, it will generally have a relatively high SOFP on the other reference IR scale.

This memorandum

- describes a method for estimating the relative reactivity of products using IR scales, where IR = [lb O_3 produced] / [lb VOC consumed] under a theoretical set of prescribed conditions,
- compares the relative contribution of individual VOCs to SJV O_3 formation potentials in 2007 and 1990,
- compares the relative O_3 formation potential of high VOC-emitting products used in the SVJ during 1990 and 2007, and
- compares the MIR and EBIR scales for describing relative O_3 formation potential.

2. METHOD FOR ESTIMATING THE REACTIVITY OF PESTICIDE PRODUCTS USING INCREMENTAL REACTIVITIES

A. Compilation of Statements of Formulas

As previously reported in Part 1 (Oros and Spurlock, 2010), Confidential CSFs were compiled for top VOC-emitting nonfumigant products in the SJV for the 1990 and 2007 May–October ozone seasons. The final data set for comparing TGA- and CSF-estimated EPs consisted of 72 primary registration numbers representing 200 total products, of which 134 were in one or both of the 1990 and 2007 inventories. Including fumigants, composition data were available for 59% and 70% of 1990 and 2007 VOC mass emissions (Table 1).

Table 1. Mass emissions (tons per day), ozone formation potential under MIR conditions (MIR OFP and ozone formation potential under EBIR conditions (EBIR OFP) for fumigants, speciated nonfumigant products and "unspeciated nonfumigant" products.

Product Group	VOC mass emissions (tpd)[1]	fraction of mass emissions	MIR OFP (tpdoe)[2]	EBIR OFP (tpdoe)[2]
1990				
fumigants	5.54	0.27	0.68	0.40
speciated nonfumigants	6.63	0.32	25.36	5.25
unspeciated nonfumigants[3]	8.35	0.41	32.88	6.83
Total	**20.52**		**58.91**	**12.47**
2007				
fumigants	6.12	0.36	10.34	2.73
speciated nonfumigants	5.84	0.34	24.16	4.74
unspeciated nonfumigants[3]	5.27	0.31	20.74	4.31
Total	**17.23**		**55.24**	**11.78**

[1] tpd = tons per day during May 1 - Oct 31 ozone season in SJV. Mass emissions of "speciated nonfumigants" includes sum of speciated products plus all related subregistrations and label revisions that share the same EPA registration number (see text for explanation).
[2] OFP = ozone formation potential, tons ozone equivalents per day (tpdoe).
[3] unspeciated nonfumigant products are those whose CSFs have not been analyzed OR did not have complete reactivity data for major volatile components. The OFPs for this group were calculated using Eq. 3.

The TGA EPs for some of these products were in error due to failure to account for water in the end use product (Oros and Spurlock, 2010), while a few other products contained components for which there were no available reactivity data. These were removed from the current analysis, leaving 65 primary registration numbers representing 190 total products, of which 128 were in one or both of the 1990 and 2007 inventories.

B. Speciation and Emission Potentials

The potential for solid or liquid-based pesticide products to emit VOCs is experimentally measured by TGA (DPR, 1994). TGA measures the percentage of product volatilized under a prescribed set of conditions, and that percentage (the EP; Spurlock, 2002) is assumed to represent the maximum potential volatilization in the field. DPR generally requires registrants to provide TGA analysis for newly registered liquid products. TGA measured EPs for individual products were obtained from DPR's emission inventory database. Details of TGA method development, method validation and inter-laboratory comparisons are described in Marty et al. (2010).

Speciation refers to the identification of individual volatile components in VOC emissions of a pesticide product. The method developed here has been previously described (Oros and Spurlock, 2010). Briefly, individual product components were identified from product CSFs. An operational vapor pressure (VP) cut-off of 0.05 Pa was used to distinguish 'volatile" components under TGA analysis conditions from "nonvolatile" components. As a test of this procedure, the mass fraction of volatile components was summed to give estimated product EPs, and these were compared to TGA-measured EPs. The CSF-estimated EPs and TGA-measured EPs were highly correlated ($r = 0.94$), with a regression slope of 0.99 (0.91, 1.08; 95%CI) and an intercept not significantly different than zero (-0.91, -5.7, 3.9; 95% CI). Based on that analysis, Oros and Spurlock (2010) concluded 0.05 Pa was a reasonable approximate estimate for distinguishing between volatile and nonvolatile components under TGA conditions. They also suggested that additional CSF analysis for a larger universe of products would be appropriate to develop a more accurate VP cutoff.

For fumigants, CSFs were not generally required for speciation because "inerts" are usually a negligible portion of a product. In these cases, the active ingredient (e.g. chloropicrin, methyl bromide and/or 1,3-D) are the volatile portion of the product. For products that generate methyl isothiocyanate (MITC) such as metam-sodium or metam potassium products, emissions are expressed on an "MITC" equivalent basis. For sodium tetrathiocarbonate, emissions are similarly expressed on an carbon disulfide basis.

C. Reactivity Scale Assignments

Product SOFPs were calculated using reactivities derived from a SAPRC-07 chemical mechanism for the MIR and EBIR scales (Carter, 2009a). Solvent mixtures such as aromatic 100, aromatic 150 and aromatic 200 are used in many pesticide products. A system of 24 "bins" for hydrocarbons has been developed that provides MIRs for mixtures based on their volatility and the chemical classes that they contained (e.g., aromatics or cycloalkanes) (Carter, 2009b). Commonly used petroleum based solvent mixtures for which bin assignments have been made include aromatic 100 (Bin 22), aromatic 150 (Bin 23) and aromatic 200 (Bin 24) (Carter, 2009b).

D. Calculations

As previously discussed, IR describe the *relative* O_3 formation potential of individual chemicals (or mixtures of similar chemicals). SOFP is the relative ability of that pesticide product to contribute to ozone formation expressed as O_3 equivalents on a "per mass product" basis ([lb O_3] / [lb product]).

$$[1] \qquad SOFP = \frac{\sum_i (f_i \times IR_i)}{\sum_i f_i} \times EF_{product}$$

where the IR_i are the individual volatile component incremental reactivities (lbs O_3/lbs VOC) defined relative to a chosen reference reactivity scale (e.g. MIR or EBIR), f_i = speciation fraction = mass fraction of the ith VOC component in the product, and EF is the mass emission fraction of the product = EP/100 ($0 \leq EF \leq 1$). SOFPs are appropriate for comparing *relative* formation potentials of different products on a per mass product basis.

For a pesticide product application or series of applications, the ozone formation potential (OFP) represents the reactivity weighted emissions expressed in terms of MIR O_3 equivalents or EBIR O_3 equivalents, again depending on chosen reactivity scale.

$$[2] \qquad OFP = lbs\ applied \times AMAF \times SOFP$$

Where AMAF = application method adjustment factor ([lb VOC emitted] / [lb VOC in product]; Barry et al., 2007). The AMAF is typically assumed 1 for nonfumigants such as emulsifiable concentrates. Like the SOFP, the OFP depends on the reference reactivity scale chosen and is appropriate for comparing *relative* ozone formation potential among years, application sites or regions. In this paper we use units for OFP of "lbs O_3 equivalents" or "tons per day O_3 equivalents" (tpdoe). In the latter case, the OFP refers to the reactivity weighted emissions averaged over the six month May – October O_3 season.

3. EMISSIONS AND OZONE FORMATION POTENTIAL

A. 1990 and 2007 San Joaquin Valley Ozone Seasons

OFPs were calculated for three classes of pesticide products: fumigants, speciated nonfumigant products, and the remainder of the inventory consisting of "unspeciated nonfumigants." These unspeciated nonfumigant products accounted for 41% and 31% of total ozone season mass emissions in 1990 and 2007, respectively (Table 1). OFPs for the unspeciated products were estimated using Equation 3, where the first term is the mean with-in product sum of composition weighted component reactivities (lbs O_3 equivalents/lbs VOC emitted), and the second term is each product's total mass emissions in the respective years.

$$[3] \qquad OFP_{nonspeciated} \cong \left[\frac{\sum_i (f_i \times IR_i)}{\sum_i f_i}\right]_{mean,speciated\ nonfumigants} \times tpd\ emissions$$

Equation 3 essentially assumes that the overall reactivity of unspeciated mass emissions is equivalent to the mean reactivity of the speciated product emissions. Based on t-tests, the mean product component reactivities (1st term in Equation 3) were not significantly different between years for the MRI scale ($p = 0.53$) or the EBIR scale ($p=0.54$). This was not surprising because of extensive product overlap between the two years. Consequently the overall mean product reactivities calculated across all 65 primary registration numbers were used for both years. These were 3.94 (lbs MIR O_3 equivalents/lbs VOC emitted), and 0.818 (lbs EBIR O_3 equivalents/lbs VOC emitted).

SJV ozone season adjusted pesticide VOC mass emissions were approximately 15% lower in 2007 than in 1990 (Table 1). This was due largely to decreases in nonfumigant emissions; 2007 fumigant emissions increased only slightly from 1990. Similarly, the total pesticide OFPs also decreased in 2007 as compared to 1990, albeit at a slightly lower amount of about 6%. This was the case for both reference reactivity scales. However, there was a clear change in the relative contribution of fumigant and nonfumigant total OFP between the two years. The 2007 fumigant OFP demonstrated a sharp increase relative to 1990, while the estimated nonfumigant OFP demonstrated a concomitant decrease by nearly the same amount (Table 1). The reason for the increase in 2007 total fumigant OFP is evident from the product component use/reactivity data.

B. Pesticide Product Component Incremental Reactivities

Changes in fumigant use between 1990 and 2007 included a sharp decrease in methyl bromide use, with concommitant increases in both MITC generating fumigants and 1,3-D (Table 2). The impact of these changes on annual OFP is clear from the IR of the fumigants. Methyl bromide has a very low reactivity, while MITC and especially 1,3-D have much larger IRs (Table 2).

Table 2. Estimated adjusted mass emissions and ozone formation potentials for pesticide product components during 1990 and 2007 May - October ozone seasons in the San Joaquin Valley. Ozone formation potentials were calculated using MIR and EBIR scale data as reported by Carter (2009).

Pesticide Component[1]	1990 Adjusted Emissions		2007 Adjusted Emissions		Incremental Reactivities[2]		1990 MIR OFP	2007 MIR OFP	1990 EBIR OFP	2007 EBIR OFP
	(lb)	(tpd)	(lb)	(tpd)	MIR	EBIR	(tpdoe)	(tpdoe)	(tpdoe)	(tpdoe)
Fumigants										
Methyl isothiocyanate	423,323	1.157	1,013,109	2.768	0.31	0.184	0.359	0.858	0.213	0.509
1,3-Dichloropropene	0	0	793,990	2.169	4.19	0.913	0.000	9.090	0.000	1.981
Methyl bromide	1,553,733	4.245	352,918	0.964	0.02	0.007	0.076	0.017	0.030	0.007
Chloropicrin	48,912	0.134	74,763	0.204	1.80	1.145	0.241	0.368	0.153	0.234
Carbon disulfide (sodium tetrathiocarbonate)	209	0.001	6,263	0.017	0.23	0.123	0.000	0.004	0.000	0.002
Dazomet breakdown products	0	0	26	0.000	na	na	----	----	----	----
Nonfumigant Active Ingredients										
Butylate	60,902	0.166	933	0.003	na	na	----	----	----	----
Molinate	34,123	0.093	1,971	0.005	1.43	0.438	0.133	0.008	0.041	0.002
Pebulate	97,801	0.267	0	0	1.58	0.470	0.422	0.000	0.126	0.000
Phorate	43,654	0.119	3,644	0.010	na	na	----	----	----	----
S-Ethyl dipropylthiocarbamate (EPTC)	213,848	0.584	33,916	0.093	1.58	0.511	0.923	0.146	0.299	0.047
Acrolein	132,621	0.362	145,399	0.397	7.24	1.600	2.623	2.876	0.580	0.636
Naled	152,074	0.416	35,625	0.097	na	na	----	----	----	----
Mevinphos	22,119	0.060	14	0.000	na	na	----	----	----	----
Cycloate	16,500	0.045	367	0.001	na	na	----	----	----	----
Oxamyl	6,794	0.019	21,844	0.060	na	na	----	----	----	----
Nonfumigant Formulation Components										
Aliphatic hydrocarbons (IRs from BIN 7)	50017.09281	0.137	17556.3217	0.048	0.684	0.157	0.093	0.033	0.021	0.008
Aromatic 100 (IRs from BIN 22)	688,924	1.882	467,345	1.277	7.38	1.284	13.891	9.424	2.417	1.640
Aromatic 150 (IRs from BIN 23)	136,714	0.374	215,536	0.589	6.66	1.240	2.488	3.922	0.463	0.730
Aromatic 200 (IRs from BIN 24)	14,046	0.038	691,892	1.890	3.74	0.680	0.144	7.070	0.026	1.285
2-Butoxyethanol	0	0	7,688	0.021	2.78	0.766	0	0.058	0	0.016
Butyrolactone	5,402	0.015	0	0	0.90	0.388	0.013	0	0.006	0
Cyclohexanol	123,048	0.336	1,150	0.003	1.84	0.642	0.619	0.006	0.216	0.002
Cyclohexanone	82,148	0.224	115,840	0.317	1.26	0.437	0.283	0.399	0.098	0.138
Ethanol	35,647	0.097	1	0.000	1.45	0.571	0.141	0.000	0.056	0.000
Ethylene glycol	56,959	0.156	817	0.002	3.01	0.999	0.468	0.007	0.155	0.002
Hexanol	42,571	0.116	44,107	0.121	2.56	0.819	0.298	0.309	0.095	0.099
Isopropanol	218,465	0.597	270,262	0.738	0.59	0.255	0.352	0.436	0.152	0.188
Kerosene	38,562	0.105	257	0.001	1.46	0.300	0.154	0.001	0.032	0.000
d-Limonene	0	0	10,044	0.027	4.40	0.947	0	0.121	0	0.026
Methanol	15,254	0.042	9,757	0.027	0.65	0.197	0.027	0.017	0.008	0.005
Methyl isobutyl ketone	0	0	12,449	0.034	3.74	1.064	0	0.127	0	0.036
N-methyl-2-pyrrolidone	0	0	91,312	0.249	2.28	0.694	0	0.569	0	0.173
Methyl salicylate (wintergreen)	12,516	0.034	344	0.001	na	na	----	----	----	----
Monochlorobenzene	33,353	0.091	0	0	0.31	-0.069	0.028	0	-0.006	0
Propylene glycol	191,287	0.523	20,307	0.055	2.48	0.750	1.296	0.138	0.392	0.042
Propylene glycol methyl ether	7,927	0.022	53,796	0.147	2.33	0.850	0.050	0.342	0.018	0.125
Stoddard solvent (IRs from BIN 15)	0	0	6,659	0.018	1.48	0.280	0	0.027	0	0.005
Triacetin	0	0	6,634	0.018	0.51	0.185	0	0.009	0	0.003
Xylene (IRs are mean of *o*-, *m*-, *p*-xylene)	124,914	0.341	28,446	0.078	9.52	1.490	3.249	0.740	0.509	0.116

[1]Fumigant and nonfumigant active ingredient emission data calculated from total use of individual active ingredients. Nonfumigant formulation component emission data calculated from use of speciated nonfumigant products and their respective subregistrations and label revisions. The mass emission data above account for approximately 67% and 70% of 1990 and 2007 adjusted mass emissions, respectively, during the May-Oct San Joaquin Valley ozone season.

[2]MIR is maximum Incremental reactivity scale, EBIR is equal benefit reactivity scale. Units for both are lbs O_3/lbs VOC. "tpdoe" is tons per day ozone equivalents. na = not available

Consequently, the fumigant contribution to overall 2007 OFP increased by more than an order of magnitude in spite of comparable total fumigant use in the two years. The increase in fumigant OFP was driven largely by 1,3-D.

The speciated nonfumigant products accounted for approximately 40 - 50% of nonfumigant mass emissions in both 1990 and 2007 (Table 1). Based on the speciated products, the largest contributors to nonfumigant ozone potential in both years are the aromatic solvents commonly used in formulating products (aromatic 100, aromatic 150, aromatic 200). A large contribution from the widely used aquatic herbicide acrolein is also evident. Assuming the products speciated each year are representative of the unspeciated nonfumigants, total mass emissions of the aromatic mixtures were amore than 60% greater in 2007 as compared to 1990. However, their contribution to pesticide OFP only increased by about 24%, from 16.5 MIR tpdoe to 20.4 MIR tpdoe in 1990 to 2007 (Table 2). The smaller net increase in OFP was attributable to a shift from use of aromatic 100 in formulating products to less reactive aromatic 150 and aromatic 200. This shift in use to heavier aromatic solvents is also consistent with anecdotal information from registrants.

C. Individual product specific ozone formation potential of a products

SOFPs describe the relative ability of a product to contribute to ozone formation on a “per lb product” basis. As expected from the wide range of component reactivities and product compositions, SOFPs are highly variable (Figure 1, Tables 3 and 4). Part of the variation is related to product formulation (Figure 2) where, for instance, emulsifiable concentrates generally contain a relatively high fraction of solvents and dry formulations do not.

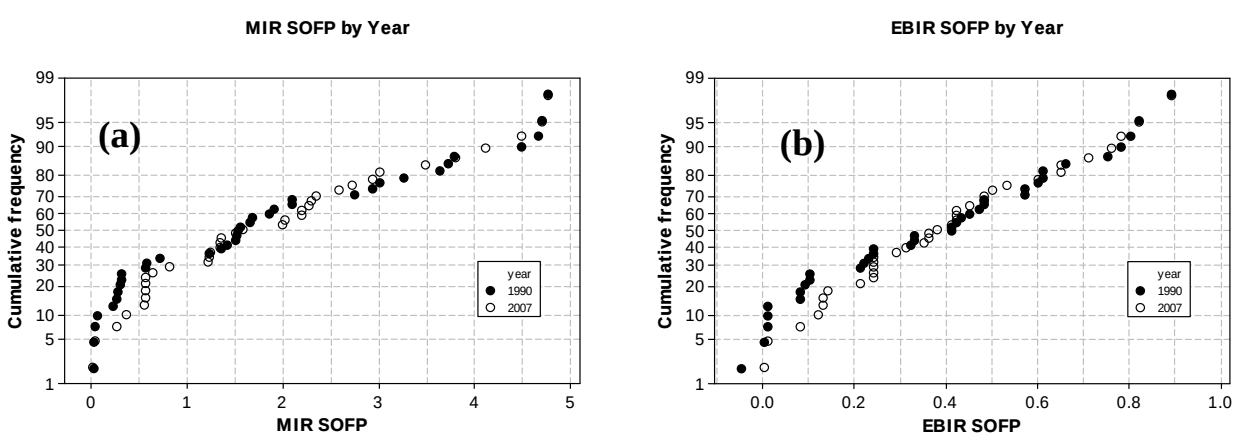

Figure 1. Cumulative frequency of 1990 and 2007 products SOFP (lbs O_3/lbs product) on (a) MIR scale and (b) EBIR scale.

Table 3. 1990 San Joaquin Valley Ozone Season Use and Ozone Formation Potentials for speciated nonfumigant products.

EPA REG NO	REPRESENTATIVE PRODUCT	Type	Primary Active Ingredient	MIR SOFP	EBIR SOFP	Ozone Season Total Use (tpd)	MIR OFP (tpdoe)	EBIR OFP (tpdoe)
3125-282	DEF 6 EMULSIFIABLE DEFOLIANT	EC	S,S,S-TRIBUTYL PHOSPHORO	1.90	0.33	3.09	5.88	1.03
2749-41	DIMETHOGON 267 EC	EC	DIMETHOATE	2.92	0.61	1.07	3.12	0.65
707-174	GOAL 1.6E HERBICIDE	EC	OXYFLUORFEN	3.63	0.61	0.65	2.37	0.40
264-418	PREP PLANT REGULATOR FOR COTTON	EC	ETHEPHON	0.02	0.00	2.06	0.05	0.01
279-2924	THIODAN 3EC INSECTICIDE	EC	ENDOSULFAN	4.48	0.78	0.43	1.91	0.33
400-89	OMITE-6E	EC	PROPARGITE	1.22	0.21	1.31	1.60	0.28
7969-58	POAST	EC	SETHOXYDIM	4.76	0.89	0.28	1.32	0.24
3125-280	MONITOR 4 LIQUID INSECTICIDE	EC	METHAMIDOPHOS	1.35	0.41	0.81	1.10	0.33
3125-283	NEMACUR 3 EMULSIFIABLE SYSTEMIC	EC	FENAMIPHOS	3.00	0.60	0.30	0.91	0.18
264-498	FOLEX 6EC COTTON DEFOLIANT	EC	S,S,S-TRIBUTYL PHOSPHORO	1.85	0.32	0.37	0.69	0.12
400-104	COMITE	EC	PROPARGITE	0.03	0.01	2.68	0.08	0.03
10182-104	FUSILADE 2000 HERBICIDE	EC	FLUAZIFOP-P-BUTYL	2.74	0.47	0.19	0.53	0.09
10182-158	TILLAM 6-E SELECTIVE HERBICIDE	EC	PEBULATE	1.50	0.42	0.33	0.50	0.14
10182-220	EPTAM 7-E SELECTIVE HERBICIDE	EC	EPTC	1.54	0.48	0.31	0.47	0.15
10182-223	ERADICANE 6.7-E SELECTIVE HERBICIDE	EC	EPTC	1.52	0.48	0.30	0.46	0.14
34704-489	CLEAN CROP DIMETHOATE 2.67 EC	EC	DIMETHOATE	4.70	0.82	0.09	0.42	0.07
100-607	RIDOMIL 2E	EC	METALAXYL	3.71	0.80	0.09	0.32	0.07
10163-99	GOWAN TRIFLURALIN 5	Liq	TRIFLURALIN	1.65	0.33	0.19	0.31	0.06
618-97	ZEPHYR 0.15 EC	EC	ABAMECTIN	1.41	0.45	0.21	0.30	0.10
352-470	DU PONT BLADEX 4L HERBICIDE	Liq	CYANAZINE	0.31	0.10	0.93	0.29	0.10
241-145	THIMET 15-G SOIL AND SYSTEMIC	Dry	PHORATE	0.30	0.10	0.52	0.15	0.05
275-61	PRO-GIBB 4% LIQUID CONCENTRATE	EC	GIBBERELLINS	0.56	0.24	0.47	0.26	0.11
279-3014	POUNCE 3.2 EC	EC	PERMETHRIN	3.78	0.66	0.07	0.25	0.04
5905-248	DIAZINON AG500 INSECTICIDE	EC	DIAZINON	3.25	0.57	0.08	0.25	0.04
10182-222	SUTAN + 6.7-E SELECTIVE HERBICIDE	EC	BUTYLATE	1.67	0.57	0.17	0.28	0.09
400-82	OMITE-30W	Dry	PROPARGITE	0.05	0.01	5.01	0.23	0.07
45639-5	NORTRON EC	EC	ETHOFUMESATE	4.66	0.75	0.06	0.28	0.05
400-278	DREXEL DIMETHOATE 2.67 EC	EC	DIMETHOATE	2.08	0.41	0.12	0.25	0.05
42697-1	SAFER INSECTICIDAL SOAP CONCENTRATE	EC	POTASH SOAP	0.57	0.22	0.32	0.19	0.07
3125-123	GUTHION 2S EMULSIFIABLE INSECTICIDE	EC	AZINPHOS-METHYL	2.09	0.43	0.07	0.15	0.03
10182-174	ORDRAM 10-G	Dry	MOLINATE	0.27	0.08	0.55	0.15	0.05
400-112	VITAVAX-200 FLOWABLE FUNGICIDE	Liq	THIRAM	0.71	0.24	0.20	0.15	0.05
524-314	LASSO HERBICIDE	EC	ALACHLOR	1.51	0.23	0.09	0.13	0.02
100-620	CAPAROL 4L	Liq	PROMETRYN	0.29	0.09	0.31	0.09	0.03
707-202	KELTHANE MF AGRICULTURAL MITICIDE	EC	DICOFOL	0.02	0.01	3.17	0.06	0.03
10182-219	DEVRINOL 2-E SELECTIVE HERBICIDE	EC	NAPROPAMIDE	0.22	-0.05	0.09	0.02	0.00
352-372	DU PONT VYDATE L	Liq	OXAMYL	0.25	0.08	0.08	0.02	0.01

Table 4. 2007 San Joaquin Valley Ozone Season Use and Ozone Formation Potentials for speciated nonfumigant products.

EPA REG NO	REPRESENTATIVE PRODUCT	Type	Primary Active Ingredient	MIR SOFP	EBIR SOFP	Ozone Season Total Use (tpd)	MIR OFP (tpdoe)	EBIR OFP (tpdoe)
62719-220	LORSBAN-4E	EC	CHLORPYRIFOS	2.71	0.48	3.79	13.50	2.45
62719-424	GOAL 2XL	EC	OXYFLUORFEN	2.19	0.42	1.21	2.67	0.51
67760-28	NUFOS 4E	EC	CHLORPYRIFOS	3.48	0.65	0.31	1.10	0.20
7969-58	POAST	EC	SETHOXYDIM	4.76	0.89	0.20	0.96	0.18
59639-35	DANITOL 2.4 EC SPRAY	EC	FENPROPATHRIN	4.10	0.76	0.17	0.69	0.13
400-89	OMITE-6E	EC	PROPARGITE	1.22	0.21	0.53	0.64	0.12
62719-250	TENKOZ TRIFLURALIN 4	EC	TRIFLURALIN	2.01	0.36	0.29	0.59	0.11
264-652	RELY HERBICIDE	EC	GLUFOSINATE-AMMONIUM	0.35	0.13	1.47	0.57	0.20
62719-79	LOCK-ON INSECTICIDE	EC	CHLORPYRIFOS	1.57	0.24	0.40	0.47	0.07
34704-489	CLEAN CROP DIMETHOATE 2.67 EC	EC	DIMETHOATE	4.70	0.82	0.10	0.46	0.08
66222-46	TRIFLUREX HFP	Liq	TRIFLURALIN	2.92	0.53	0.15	0.43	0.08
279-2924	THIONEX (ENDOSULFAN) 3EC	EC	ENDOSULFAN	4.48	0.78	0.09	0.39	0.07
66222-28	GALIGAN 2E OXYFLUORFEN HERBICIDE	EC	OXYFLUORFEN	2.34	0.45	0.16	0.39	0.07
100-898	AGRI-MEK 0.15 EC MITICIDE/INSECTICIDE	EC	ABAMECTIN	1.33	0.42	0.29	0.38	0.12
51036-198	DIMETHOATE 267	EC	DIMETHOATE	2.28	0.50	0.16	0.37	0.08
352-515	DU PONT ASANA XL INSECTICIDE	Liq	ESFENVALERATE	0.81	0.14	0.44	0.35	0.06
51036-110	DIMETHOATE 4E	EC	DIMETHOATE	1.23	0.31	0.43	0.35	0.11
5481-479	DIBROM 8 EMULSIVE	EC	NALED	2.19	0.38	0.14	0.31	0.06
100-816	DUAL MAGNUM HERBICIDE	EC	S-METOLACHLOR	0.63	0.12	0.46	0.29	0.05
3125-283	NEMACUR 3 EMULSIFIABLE SYSTEMIC	EC	FENAMIPHOS	3.00	0.60	0.08	0.28	0.05
68292-2	WEEDAXE HERBICIDE	EC	2,4-D, DIMETHYLAMINE	1.50	0.35	0.13	0.25	0.06
66222-60	ARROW 2 EC HERBICIDE	EC	CLETHODIM	3.79	0.71	0.06	0.21	0.04
66222-19	CHLORPYRIFOS 4E AG	EC	CHLORPYRIFOS	1.98	0.36	0.10	0.19	0.03
10163-220	MSR SPRAY CONCENTRATE	EC	OXYDEMETON-METHYL	2.57	0.65	0.07	0.18	0.05
34704-207	CLEAN CROP DIMETHOATE 400	EC	DIMETHOATE	1.21	0.29	0.15	0.18	0.04
400-104	COMITE	EC	PROPARGITE	0.03	0.01	0.79	0.17	0.03
55146-62	GIBGRO 4LS	Liq	GIBBERELLINS	0.55	0.24	0.30	0.17	0.07
100-897	ZEPHYR 0.15EC	EC	ABAMECTIN	1.33	0.42	0.11	0.15	0.05
19713-232	DREXEL DIMETHOATE 2.67	EC	DIMETHOATE	2.26	0.48	0.06	0.13	0.03
3125-280	MONITOR 4 LIQUID INSECTICIDE	EC	METHAMIDOPHOS	1.35	0.41	0.08	0.11	0.03
73049-15	PRO-GIBB 4% PLANT GROWTH REGULATOR	Liq	GIBBERELLINS	0.56	0.24	0.19	0.11	0.05
62097-2	FALGRO 4L	Liq	GIBBERELLINS	0.55	0.24	0.15	0.08	0.04
275-61	PRO-GIBB 4% LIQUID CONCENTRATE	EC	GIBBERELLINS	0.56	0.24	0.10	0.05	0.02
70506-6	TENGARD SFR ONE SHOT TERMITICIDE	EC	PERMETHRIN	0.54	0.13	0.07	0.04	0.01
2935-366	SEVIN 5 BAIT	Dry	CARBARYL	0.00	0.00	0.68	0.03	0.01
352-372	DU PONT VYDATE L	Liq	OXAMYL	0.25	0.08	0.07	0.02	0.00

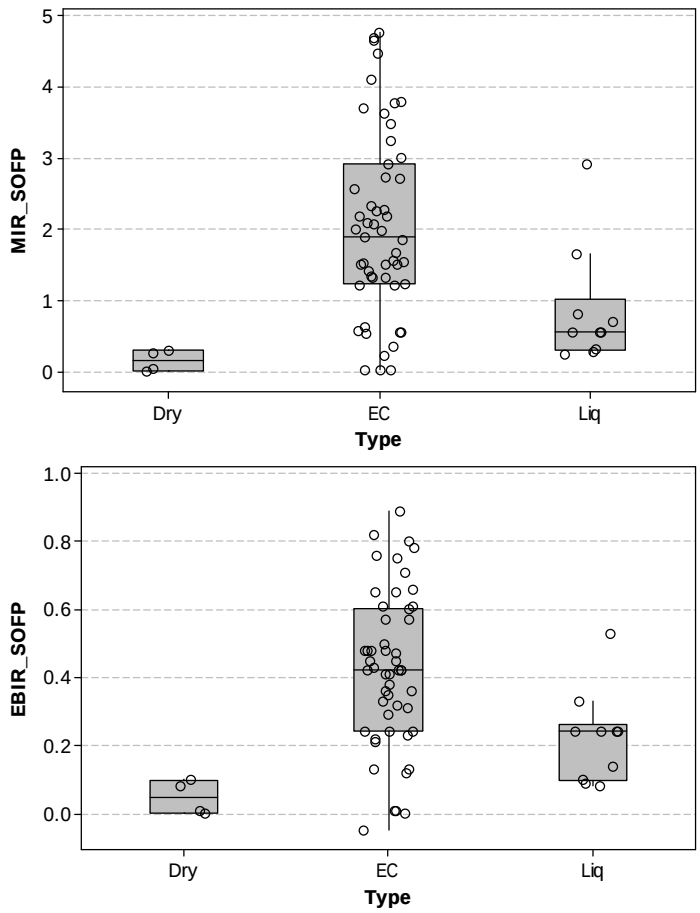

Figure 2. MIR and EBIR SOFPs (lbs O_3/lbs product) for ECs), other liquid formulations (LIQ) and dry formulations (DRY) such as wettable powders and granulars.

D. Reactivity Scales

As previously noted, MIRs have been developed from chamber data under high NOx conditions where changes in VOC levels have the greatest possible impact on ozone formation. In contrast, under EBIR conditions, changes in either VOC (i.e. the base VOC mixture) or NOx concentrations have equal impacts on O_3 formation. Thus, MIR conditions are more representative of urban airsheds, while EBIR might be more representative of rural airsheds. DPR's stakeholders have expressed concern over use of the MIR scale, arguing that "MIR's that have been established for urban airsheds have very limited significance to the SJV NAA and other rural airsheds" because these "rural agricultural airsheds are more likely to be NOx-limited" (Spurlock and Oros, 2009). DPR responded by noting that the DPR "does not model or estimate

actual ozone formation," and reminding stakeholders that the pesticide element of the 1994 SIP requires DPR to "achieve VOC emission reductions *relative* to the 1990 base year (where the VOC emissions may be adjusted for reactivity if such information exists)." Thus DPR's primary interest is in *relative* reactivity of pesticide products as opposed to quantitatively estimating actual O3 formation.

Figure 3 illustrates the relationship between SOFPs calculated using both scales for 65 primary registration numbers. The high correlation between product SOFPs calculated using the two IRs demonstrates that *relative* comparisons between SOFPs and, by extension, OFPs, will yield generally similar results. Consequently, the question of which reactivity scale to use is not a critical issue.

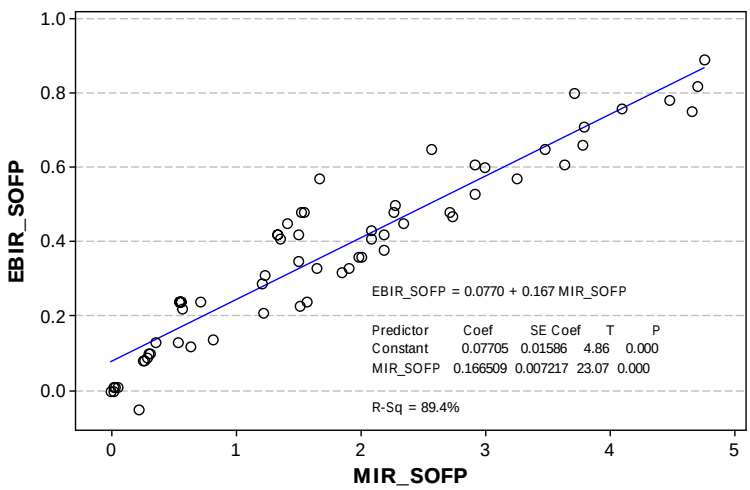

Figure 3. Comparison of product SOFPs calculated using the MIR and EBIR scales.

4. CONCLUSION

The preceding memorandum (Oros and Spurlock, 2010) and this report provide the outline of a scientifically defensible method to incorporate reactivity into DPR's current mass-based VOC inventory. Additional work remains, including more accurate characterization of certain component reactivities [e.g. aromatics (Carter, 2009a; selected semi-volatile active ingredients; Table 2], additional analysis of pesticide product CSFs and TGA data to explicitly speciate a larger portion of the inventory, and additional analysis to refine the current vapor pressure cutoff (0.05 Pa) used to discriminate between volatile and nonvolatile product components.

While scientifically feasible, DPR would need to make several administrative and regulatory revisions to account for reactivity in its VOC inventory. This includes creating and maintaining

an electronic database of information in CSFs, and revising the pesticide element of the SIP. These administrative and regulatory aspects of incorporating reactivity into the pesticide VOC inventory are beyond the scope of this evaluation.

5. REFERENCES

Barry, T., Spurlock, F. and Segawa, R. 2007. Pesticide Volatile Organic Compound Emission Adjustments for Field Conditions and Estimated Volatile Organic Compound Reductions-Initial Estimates. (PDF, 184 kb). Appendix 1 (PDF, 734 kb) Appendix 2 and 3 (PDF, 376 kb).

Carter, William P.L. 1994. Development of ozone reactivity scales for volatile organic compounds. *Journal of the Air and Waste Management Association*, 44: 881-899.

Carter, William P.L. 2009a. Development of the SAPRC-07 Chemical Mechanism and Updated Ozone Reactivity Scales. Final Report to the California Air Resources Board, Contract No. 03-318. June 22, 2009.

Carter, William P.L. 2009b. Appendix C. "Updated Maximum Incremental Reactivity Scale and Hydrocarbon Bin Reactivities for Regulatory Applications," Final Report to California Air Resources Board September 10, 2009. Web site: <http://www.arb.ca.gov/regact/2009/mir2009/appc.pdf>.

Carter, W.P.L. and Malkina, I.L. 2007. Investigation of Atmospheric Ozone Impacts of Selected Pesticides. Final Report to California Air Resource Board, Contract No. 04-334. January 10.

Kumar, A., Yang, W., Howard, C.J., Kleeman, M.J., Derrick, D. and Green, P.G. 2008. Assessment of the ozone formation potential from pesticide solvents using a mobile ozone chamber assay approach. *Journal of ASTM International*, Volume 5, Issue 7 (July 2008).

Marty, M., F. Spurlock and T. Barry. 2010. Volatile Organic Compounds from Pesticide Application and Contribution to Tropospheric Ozone. Chapter 19, *In*: Hayes' Handbook of Pesticide Toxicology, R. Krieger, ed., Elsevier Press.

Oros, Daniel R. 2009. Pilot Project Proposal: Estimating Pesticide Product Volatile Organic Compound Emission Speciation and Reactivity Based on Product Composition. Memorandum to Randy Segawa, Environmental Monitoring Branch, Department of Pesticide Regulation, Sacramento, California. August 17, 2009. Web site: <http://www.cdpr.ca.gov/docs/emon/vocs/vocproj/2160_segawa.pdf>.

Oros, D.R. and Spurlock, F.C. 2010. Estimating Pesticide Product Volatile Organic Compound Emission Speciation and Reactivity Based on Product Composition. Part 1. Speciating VOC Emissions using Confidential Statements of Formula.

Spurlock, F. and D. Oros. 2009. Response to stakeholder comments on pilot project proposal: estimating pesticide product volatile organic compound emission speciation and reactivity based on product composition. Memorandum to R. Segawa. Available online: <http://www.cdpr.ca.gov/docs/emon/vocs/vocproj/2159_segawa.pdf>.

Appendix 1. ABBREVIATIONS

AMAF - application method adjustment factor, ([lb VOC emitted] / [lb VOC in product])

CSF - confidential statement of formula. A confidential document listing product ingredients.

EBIR - equal benefit incremental reactivity, ([lb O_3 produced] / [lb VOC consumed]). A measure of the ability of a volatile organic chemical to form ozone under a well-defined set of conditions.

EC - emulsifiable concentrate - a type of pesticide formulation that generally contains a high percentage of solvent(s).

EF - emission fraction. Mass fraction of volatile chemicals present in a pesticide product, (lbs volatile chemicals)/(lbs product)].

EP - emission potential. Percentage of volatile chemicals present in a pesticide product, = EF x 100.

MIR - maximum incremental reactivity, ([lb O_3 produced] / [lb VOC consumed]). A measure of the ability of a volatile organic chemical to form ozone under a well-defined set of conditions.

NAA - non-attainment area. An area that has been designated by USEPA as out of attainment with federal ozone air quality standards.

NOx - oxides of nitrogen

OFP - ozone formation potential. A relative measure of reactivity-weighted mass VOC emissions. The OFP depends on the reference reactivity scale chosen and is appropriate for comparing *relative* ozone formation potential among years, application sites or regions.

SJV - San Joaquin Valley

SOFP - specific ozone formation potential. The SOFP of a product (SOFP) depends on the reference reactivity scale chosen, and reflects the relative ability of that pesticide product to contribute to ozone formation expressed as O_3 equivalents on a "per mass product" basis ([lb O_3] / [lb product]).). SOFPs are appropriate for comparing *relative* formation potentials of different products on a per mass product basis**.**

TGA - thermogravimetric analysis. A technique for measuring the volatile chemical content of mixtures such as pesticide products.

tpdoe - tons per day ozone equivalents. A measure of reactivity weighted VOC emissions. The tpdoe is defined relative to a particular reactivity reference scale (e.g. MIR, EBIR).

VOC - volatile organic compound